Asian Journal of Chemistry; Vol. 29, No. 6 (2017), 1229-1234

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2017.20440

# Synthesis and Characterization of Ion-Imprinted Polymer for Selective Adsorption of Zinc Ions in Aqueous media

G. ZUHRA MEMON[1,*], SUMERA SARWAR[1], F. MEMON[2], MUHAMMAD QASIM SAMEJO[1] and A.G.M. VASANDANI[1]

[1]Dr. M.A. Kazi Institute of Chemistry, University of Sindh, Jamshoro-76080, Pakistan
[2]Department of Physiology, University of Sindh, Jamshoro-76080, Pakistan

*Corresponding author: E-mail: zuhramemon_chem@yahoo.com

*Received*: 9 December 2016; *Accepted*: 25 February 2017; *Published online*: 10 April 2017; AJC-18331

In this study, a new zinc(II) ion imprinted polymer [Zn(II)-IIP] was synthesized by radical polymerization using using $Zn(NO_3)_2$, 4-vinylpyridine (4-VP), ethylene glycol dimethacrylate (EGDMA) and benzoyl peroxide (BPO) as the template ion, functional monomer, cross-linking agent and initiator, respectively. The prepared materials (imprinted polymers + non-imprinted polymer) were then characterized using Fourier transform infrared (FT-IR) spectroscopy and thermogravimetric analysis (TGA). These characterization methods confirmed the difference between ion imprinted polymers (IIP) and non-imprinted polymers (NIP). The imprinted Zn(II) ions were completely removed from polymer by leaching with 0.1 M HCl. The adsorption parameters such as contact time, initial concentration shaking speed and pH have been studied. Adsorption was found to be repaid within 40 min and maximum % adsorption was observed at pH 8. The Fruendlich, Langmuir and D-R models were used to study the partitioning behaviour of the adsorption systems. Using kinetics models 1$^{st}$ order rate constant (k) and $R_d$ (intra particle rate constant) have been calculated. Some thermodynamical parameters *i.e.*, studies ΔH, ΔG and ΔS have been calculated.

**Keywords: Zinc(II), Ion-imprinted polymer, 4-Vinylpyridine, Selective adsorption.**

## INTRODUCTION

Molecularly imprinted polymers (MIP's) are specialized cross-linked polymers that can exhibit high attraction and affinity towards a single target molecule, ions or metals or they can be projected to exhibit 'high selectivity' for related molecules, ions or metals [1,2]. Selective production of molecularly imprinted polymer (MIP) is due to the presence of template molecules or ions and functional monomers in the polymer synthesis [3]. Template ions or molecules removed from the polymer matrix. Therefore, molecularly imprinted polymer selectively identify the template ions from a sample [4]. The molecularly imprinted polymer is a polymer that can specifically bind to a target molecule in a highly selective manner [5]. Molecularly imprinted polymers are, easy to prepare, have stable performance and low price. Thus, the resulting molecularly imprinted polymer can be considered artificial affinity media.

Zinc is an essential trace elements on the human body, but it can be toxic at higher concentrations. It plays a significant role in the transmission function and the immune system of nerve signals [6]. Zinc can play a dual role as significant metal for humans and as a toxic element so it's complete removal is not possible. In high concentrations may cause poisoning, zinc poisoning chief indicators, including non-fatal fume fever, electrolyte imbalance, pneumonia, dizziness and incoordination muscle [7,8]. Therefore, the elimination of zinc metal compared to other heavy metals from aqueous solutions is a challenge.

Number of studies involving removal of metal ions in the ion imprinted polymers have been made [9-12] but less study has been done on zinc(II)-ion imprinted polymer. In the present study, the zinc(II)-ion imprinted polymer has been synthesized and characterized, its application in recovery of Zn(II) ions from aqueous medium was also studied.

## EXPERIMENTAL

4-Vinyl pyridine was purchased from ACROS Organics, New Jersey USA. Ethyleneglycoldimethacrylate (EGDMA), benzoyl peroxide (BPO) was purchased from (Trade TCI mart) TCI-EP Tokyo Kasei Kogyo Co. Ltd, Japan. All other chemicals were reagent grade and purchased from ACROS Organics, New Jersey USA. During the experiment, deionized water is used.

**Synthesis of zinc(II) ion imprinted and non-imprinted polymers:** In order to prepare Zn(II)-ion imprinted polymer by radical polymerization, 4 mmol of $Zn(NO_3)_2$ was dissolved

in a ethanol:water (3:1) mixture followed by the addition of 12 mmol of 4-vinylpyridine (4-VP), 60 mmol of ethylene glycol dimethacrylate (EGDMA) and 10 mg of benzoyl peroxide. The reaction mixture was sonicated, after 1 h bubbling with nitrogen for 10 min and after 1 h bubbling with nitrogen for 10 min, the reaction mixture was sonicated for 10 min and the polymerization was started at 70 °C for 24 h. After completion of the polymerization the resulting polymer was removed from the reaction tube and treated with ethanol and washed with water to remove the unreacted monomers. The polymer was mechanically grounded and sieved prior to storage. The same procedure was followed for non-imprinted polymer in the absence of template ion for removing the template molecule, molecular imprinted polymer was treated with 0.1 M HCl. The excess amount of HCl was washed with methanol. This procedure was repeated several times until the complete removal of the template ion was achieved as shown in Fig. 1.

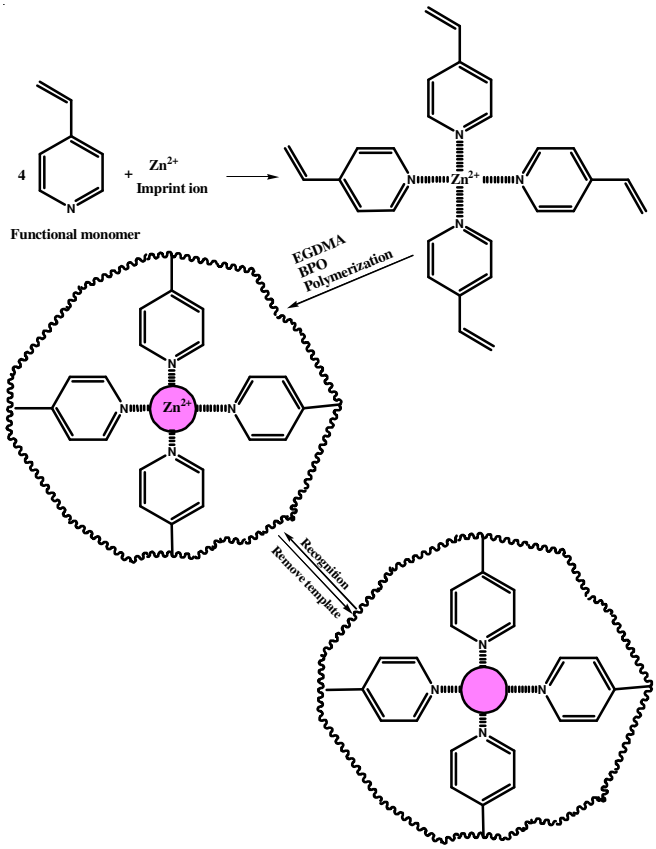


Fig. 1. Schematic illustration of imprinting process for the preparation of Zn(II)-imprinted polymer and its removal

**Batch adsorption experiment:** Batch adsorption experiments were carried out to explore the adsorption of zinc(II) ion for an aqueous solution. In each bath experiment different parameters such as pH of the medium, the dose of adsorbent, shaking speed, concentration of medium, shaking time, temperature were optimized for adsorption of Zn(II) ions. Each experiment was carried out by shaking 0.005 g of adsorbent with 10 mL of salt $Zn(NO_3)_2$ solution of preferred concentration.

At the end of the experiment, the adsorbent was removed from the solution by filtration and the filtrate was analyzed by atomic absorption spectrophotometer.

Adsorption capacity was calculated using following formula:

$$\text{Adsorption}\ (\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

whereas $C_i$ and $C_e$ are concentrations of Zn(II) ions before and after removal, respectively.

**Characterization of Zn(II) ion imprinted polymer:** FTIR spectra of Zn(II) ion imprinted polymer was taken by using FTIR spectrophotometer Nicolet 5700 Thermo Electron Corporation, USA. Thermal stability of the Zn(II) ion imprinted polymer was checked by Perkin Elmer's Diamond TG/DTA Thermal Analyzer with Pyris Manager Software by performing thermo gravimetric analysis (TGA).

## RESULTS AND DISCUSSION

**Characterization by FT-IR:** Released infrared spectrum of zinc(II)-imprinted polymer [Zn(II)-IIP] and non-imprinted polymer (NIP) material recorded using KBr pellets (Fig. 2). Area exists no band 1648-1638 $cm^{-1}$ indicates the absence of the vinyl group in polymer. This confirms the complete polymerization of the vinylpyridine. Infrared spectrum of $Zn^{2+}$ imprinted polymer has a strong characteristic stretching about 3400 $cm^{-1}$ described electrostatic interaction between $Zn^{2+}$ and pyridine groups.

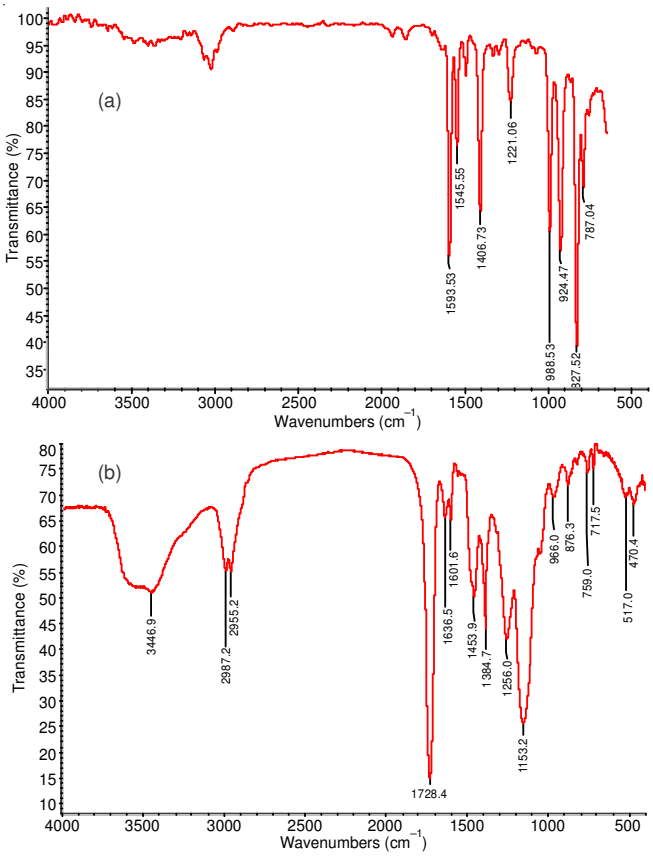


Fig. 2. FTIR spectra of (A) non-imprinted 4-vinylpyridine and (B) Zn(II)-imprinted polymer

**Characterization by TGA:** Thermal stability of Zn(II) ion imprinted polymer was checked by performing thermogravimetric analysis (Fig. 3). The results of thermogravimetric analysis showed overall remarkable stability of polymer

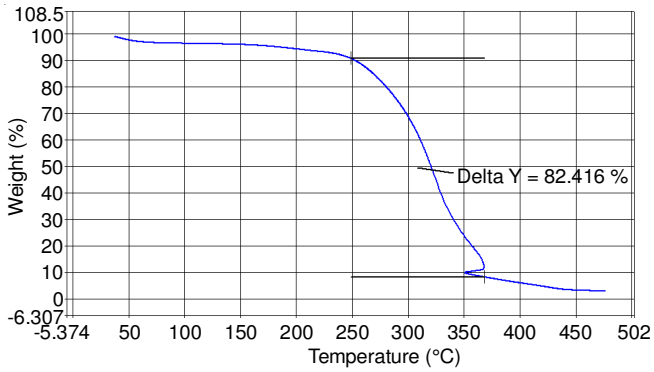


Fig. 3. Thermogram for Zn(II) ion imprinted polymer

material. It shows the major weight loss in two stages. (a) From 30-250 °C indicates that the solvent is very interactive viewing 10 % of the first phase of weight loss. (b) Weight loss of 80 % was observed from 250-370 °C due to the organic part of polymer material. The third stage of weight loss of 7 % was observed from 350-500 °C due to formation of metal oxide residue.

**Effect of pH:** During adsorption studies optimization of pH of the adsorption medium plays a significant role. The adsorption studies for Zn(II) ions was done over the range of pH 2-12 by taking 0.005 g of adsorbent per 10 mL of 5 ppm salt solution at shaking speed of 100 rpm for 30 min at room temperature. It was observed that the % adsorption increases with increasing pH as shown in Fig. 4. At lower pH the functional groups present in template selective sites was protonated due to increase in $H^+$ ion concentration. As a result the adsorbent shows lower affinity for metal ion at lower pH. In acidic pH, the lower adsorption proved that the $H^+$ ion is the competitor ions of Zn(II) ions since the nitrogen in pyridine groups in the polymer is responsible for the binding site of Zn(II) are mainly protonated [12,13]. Maximum adsorption was observed at pH 8 because at a higher pH concentration of competitor $H^+$ ions decreases and number of negatively sites increases.

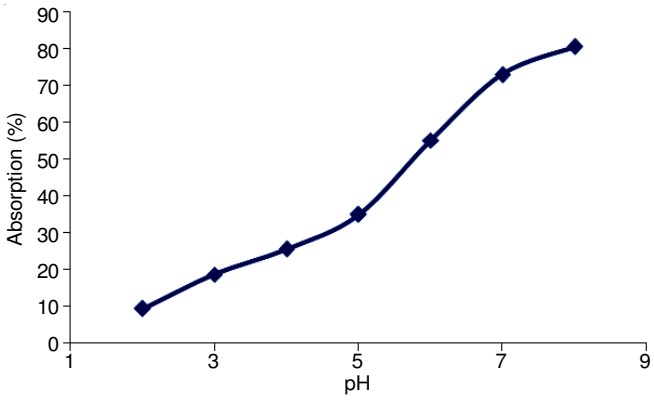


Fig. 4. Effect of pH for the adsorption of Zn(II) onto Zn(II) ion imprinted polymer

**Effect of adsorbent dose:** The amount of adsorbent is an important factor for adsorption capability of an adsorbent for metal ions (adsorbate) at a given initial concentration [14]. The study on effect of amount of adsorbent for the removal of Zn(II) ion was done by changing the amount of adsorbent in the range of 0.001-0.01 g per 10 mL of 5 ppm salt solution. As shown in Fig. 5, it was observed that % adsorption increases till 0.005 g and after that there is no significant change was observed. This shows that at certain concentration of adsorbent % adsorption increases and after that it shows no major change due to saturation of vacant sites and fixed amount of adsorbate. After 0.005 g of adsorbent % adsorption was shown almost constant.

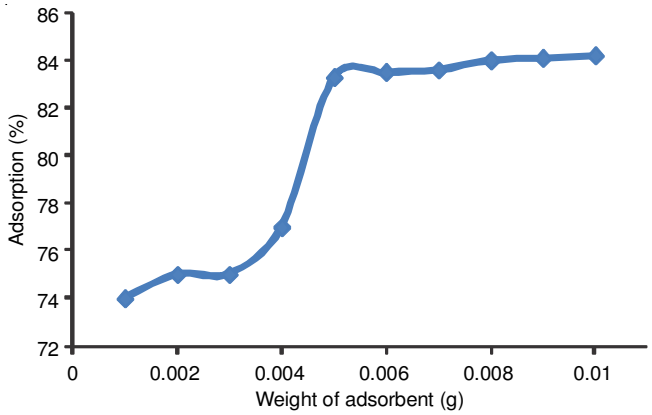


Fig. 5. Effect of adsorbent amount for the adsorption of Zn(II) onto Zn(II) ion imprinted polymer

**Effect of shaking speed:** Shaking speed is an important parameter for an adsorption capacity of an adsorbent for metal ions (adsorbate). Effect of shaking speed on adsorption of Zn(II) was studied in the range of 25-150 rpm. Fig. 6 showed that the % adsorption increases with increasing shaking speed and reaches maximum % adsorption at 100 rpm and then decreasing with increasing shaking speed. Therefore 100 rpm shaking speed was used for further studies.

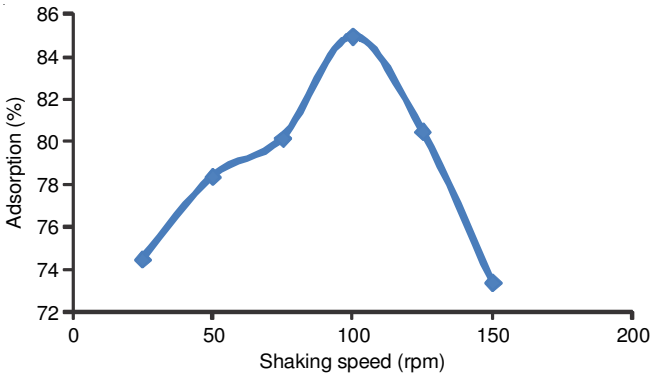


Fig. 6. Effect of shaking speed on adsorption of Zn(II) onto Zn(II) ion imprinted polymer

**Adsorption isotherms:** In adsorption studies the adsorption isotherms have a significant role to predicting adsorption systems. The adsorption isotherms are used to evaluate the equilibrium concentration of the adsorbate in bulk solution on unit weight of the adsorbent at constant temperature. Adsorption isotherms comparing the relationship between amount adsorbed per unit volume of the adsorbent and at a given temperature the concentration of adsorbed under equilibrium conditions. Freundlich, Langmuir and Dubinin-Radushkevich (D-R) isotherms have been used to analyze the equilibrium experimental data.

**Freundlich adsorption isotherm:** Freundlich adsorption isotherm is a mathematical relation that describes the exponential distribution of sites, heterogeneity of the surfaces and their energies. Freundlich adsorption isotherm can be described by the following equation:

$$\log C_{ads} = \log C_m + \frac{1}{n}\log C_e \quad (2)$$

where 1/n is related to the intensity of the characteristic absorption constant, $C_{ads}$ adsorbed amount of the adsorbate to the adsorbent (mol $g^{-1}$), $C_e$ is the equilibrium concentration of the adsorbate in solution (mol/$dm^3$) and $C_m$ is the multilayer adsorption capacity of adsorbent (mmol $g^{-1}$). A plot of log $C_{ads}$ *versus* log $C_e$ would shows in a straight line with a slope of 1/n and intercept of log $C_m$ as shown in Fig. 7 (Table-1). The value of 1/n < 1 shows that the adsorption capacity at lower equilibrium concentration is slightly reduced.

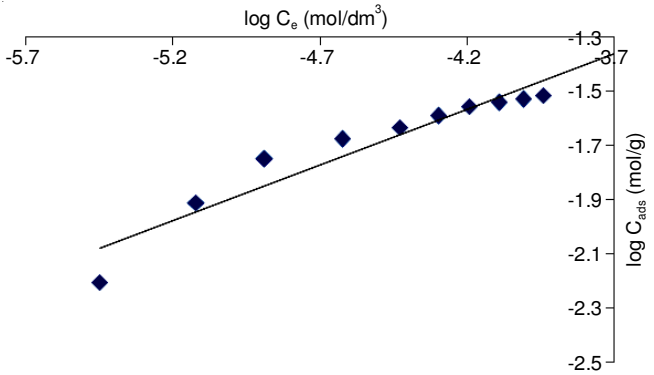


Fig. 7. Freundlich adsorption isotherm for Zn(II) on to ion imprinted polymer

TABLE-1
ISOTHERM CONSTANTS AND VALUES OF $R^2$ FOR Zn(II)

| Parameters | Value | $R^2$ |
|---|---|---|
| Freundlich isotherm | | |
| $K_F$ (mmol/g) | 1.44±0.13 | 0.92±0.002 |
| 1/n | 0.4106±0.01 | |
| Langmuir isotherm | | |
| Q (mmol/g) | 0.034±0.002 | 0.998±0.007 |
| b ($dm^3$/mol) | 73270±3.4 | |
| $R_L$ | 0.713-0.0713 | |
| Dubinin-Radushkevich isotherm | | |
| $X_m$ (mmol/g) | 0.00163±0.0002 | 0.95±0.002 |
| E (kJ/mol) | 12.91 ± 1.06 | |

**Langmuir adsorption isotherm:** In the present study the Langmuir isotherm is employed to evaluate the adsorption process. The postulates on which Langmuir isotherm is based are: (1) monolayer adsorption (2) fixed number of distinct localized active sites which are energetically uniform; (3) no interaction between the molecular species adsorbed [12,15] the linear form of Langmuir adsorption isotherm is:

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \quad (3)$$

where "b" is a constant called enthalpy of adsorption ($dm^3$ $mol^{-1}$) and "Q" is a constant called adsorption saturation capacity (mol $g^{-1}$) are independent of temperature. A plot of $C_e/C_{ads}$ *versus* $C_e$ gives a straight line with a slope of 1/Q and intercept of 1/Qb as shown in Fig. 8 and the results are listed in Table-1. A dimensionless constant $R_L$ was calculated by using the value of "b" by using this formula

$$R_L = \frac{1}{(1 + bC_i)} \quad (4)$$

where "b" is a Langmuir constant called enthalpy of adsorption and $C_i$ is initial concentration. If the value of "$0 < R_L < 1$" indicating favourable adsorption process and if the value of $R_L > 1$ indicating unfavourable adsorption process, if the value of $R_L = 0$ it means that the adsorption process is irreversible in nature [16]. The values of $R_L$ were calculated in the range of (0.713-0.00713) specifying highly favourable adsorption process.

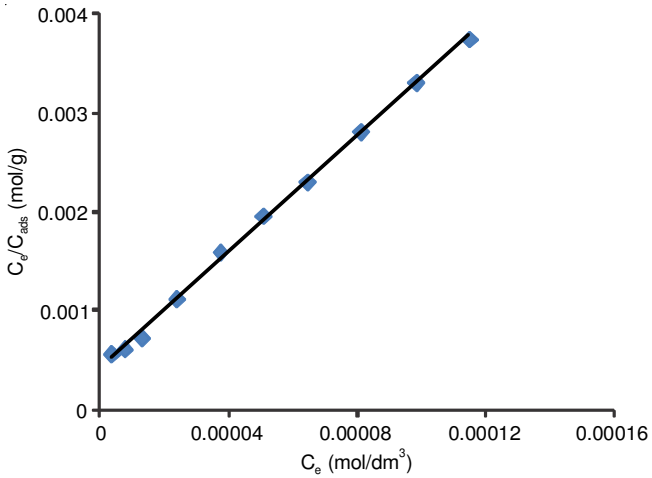


Fig. 8. Langmuir adsorption isotherm for Zn(II) on to ion imprinted polymer

**Dubinin-Radushkevich (D-R) isotherm:** Heterogeneous surface adsorption mechanism having a Gaussian energy distribution generally represented by Dubinin-Radushkevich isotherm. The Dubinin-Radushkevich model effectively fixed great solute activities and the intermediate sort of concentration data well [17].

The Dubinin-Radushkevich (D-R) model is a more generalized form of isotherm as compared with Langmuir adsorption isotherm, because it does not adopt constant adsorption potential or surface homogeneity. The linear form of Dubinin-Radushkevich (D-R) model is:

$$\ln C_{ads} = \ln X_m + \beta\varepsilon^2 \quad (5)$$

where $C_{ads}$ is the quantity of adsorbate adsorbed on the adsorbent surface in (mol $g^{-1}$) and $X_m$ is D-R constant depend on adsorption capacity, ε is Polanyi sorption potential which is calculated by using following formula:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (6)$$

where $C_e$ is the concentration in (mol/$dm^3$) of the adsorbate in solution at equilibrium and R is the general gas constant in kJ/mol. K and T is temperature (Kelvin).

Polanyi adsorption potential (ε) is the effort necessary to take away an adsorbate molecule to infinity from its position in the adsorption space and is independent of temperature [18,19]. The plot of ln $C_{ads}$ *versus* $\varepsilon^2$ gives straight line with the slope of β and the intercept of $K_{D-R}$ as shown in Fig. 9 and

results are shown in Table-1. Energy (E) per adsorbate molecule can be calculated by using following relation:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (7)$$

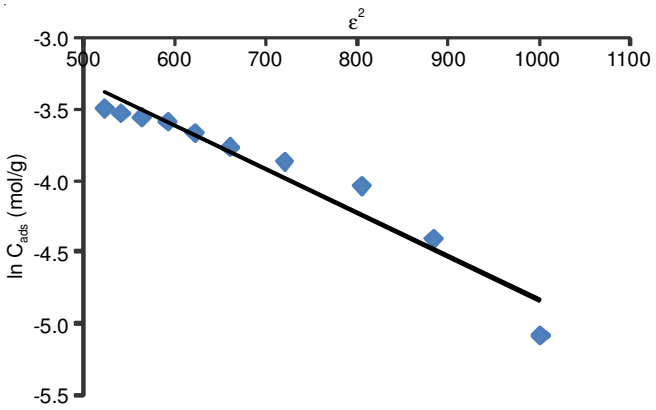


Fig. 9. Dubinin-Radushkevich adsorption isotherm for Zn(II) on to ion imprinted polymer

**Kinetic studies:** Kinetic performance of an adsorbent has great significance for its applications. By kinetic examination, the solute absorption rate determines the residence time required for the completion of the adsorption reaction. The required time for adsorption was determined in a batch experiment by shaking 0.005 g of polymer in salt solution of preferred concentration for 5-100 min. It was observed that % adsorption increases till 30 min and after that there is no major change was observed [20,21]. To investigate kinetics of adsorption of Zn(II) on Zn(II) ion imprinted polymer different kinetic models was used to test experimental data. A simple kinetic study of the adsorption is calculated using the pseudo first order equation [22,23].

$$\log (q_e - q_t) = \log q_e = \frac{k_t}{2.303} \quad (8)$$

where $q_e$ and $q_t$ ($dm^3\ g^{-1}$) are the equilibrium amounts of metal ion adsorbed on the adsorbent surface at the time and k is the pseudo-first-order rate constant of adsorption.

Fig. 10 shows the kinetic study of adsorption Zn(II) onto Zn(II) ion imprinted polymer while studying the effect of shaking time on % adsorption, the plot of log ($q_e - q_t$) *versus* shaking time gives straight line and value of the slope of the linear curve is calculated first order rate constant k, which is mentioned in Table-2.

TABLE-2
KINETIC MODEL PARAMETERS AND VALUES OF $R^2$ FOR Zn(II)

| Parameters | Values | $R^2$ |
|---|---|---|
| Lagergren model | | |
| K ($min^{-1}$) | 0.076 ± 0.00 | 0.931 ± 0.001 |
| Morris-Weber model | | |
| $R_d$ (μmol $g^{-1}$ $min^{-1}$) | 0.968 ± 0.045 | 0.995 ± 0.004 |

The kinetics of adsorption were also studied by using Morris-Weber equation [9] as follows:

$$q_t = R_d \sqrt{t} \quad (9)$$

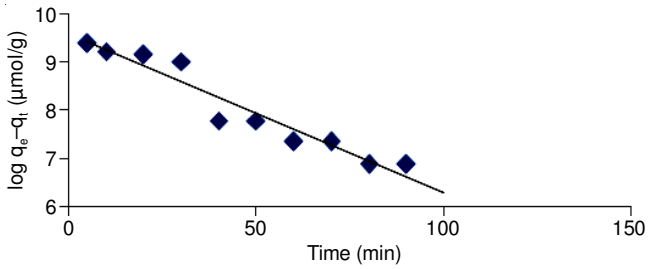


Fig. 10. Lagergren (LG) plot for Zn(II) on to ion imprinted polymer

where $R_d$ is the rate constant of intraparticle transport and $q_t$ is the adsorbed concentration at a time "t". The plot of $q_t$ *versus* $t^{1/2}$ gives straight line as shown in Fig. 11. Up to 80 min, the equation holds well, but diverges as the contact time is raised. Using the slope of the plot in the initial period the rate constant of intraparticle transport $R_d$ was calculated which is mentioned in Table-2.

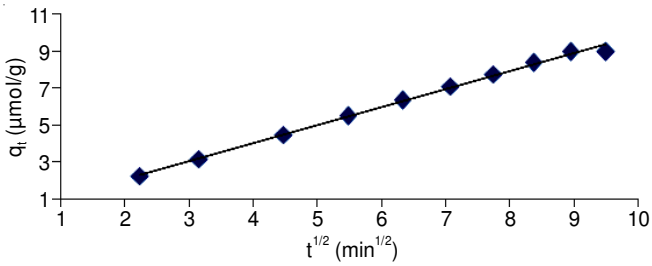


Fig. 11. Morris-Weber plot for Zn(II) on to ion imprinted polymer

Reichenberg equation is also used to study kinetics of adsorption process. It is used to explore the nature of the adsorption mechanism *via* film diffusion or intraparticle diffusion mechanism. The following form of Reichenberg equation was used:

$$B_t = -0.4977 - \ln (1 - Q) \quad (10)$$

The plot of $\beta_t$ *vs.* time (Fig. 12) follows linearity, which identifies that the adsorption process occurs through the release of the film that the linear path does not pass through the origin.

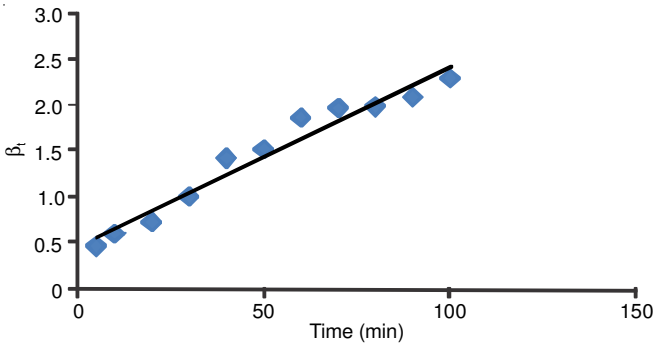


Fig. 12. Reichenberg plot for Zn(II) on to ion imprinted polymer

**Thermodynamic studies:** Thermodynamic studies of an adsorption process are used to deduce whether the process is spontaneous or non-spontaneous. The spontaneity of a chemical reaction can be indicated by Gibb's free energy change (ΔG). In order to determine the Gibb's free energy of the process, two factors enthalpy (ΔH) and entropy (ΔS) of the system must be considered [24]. The effect of temperature on adsorption

of Zn(II) on an ion imprinted polymer was studied in temperature range of 283-363 K. The value of ln $K_c$ was calculated by using van't Hoff equation [25].

$$\ln K = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (11)$$

where ΔH is enthalpy (KJ $mol^{-1}$) and ΔS is entropy (KJ $mol^{-1}$ $K^{-1}$) changes respectively. R is the general gas constant (8.314 J/mol K) and T is absolute temperature. The plot of ln K against 1/T follows linearity with a coefficient of determination ($R^2$) 0.972 ± 0.002 as shown in Fig. 13. By using intercept (ΔS/R) and slope (-ΔH/R) of plot, the values of ΔS and ΔH were calculated and ΔG was computed from following equation:

$$\Delta G = -RT \ln K \quad (12)$$

The values of thermodynamic parameters are shown in Table-3, the negative value of ΔH (-14.82 ± 1.2) and ΔS (-0.038 ± 0.003) indicating that the adsorption process is exothermic and spontaneous in nature.

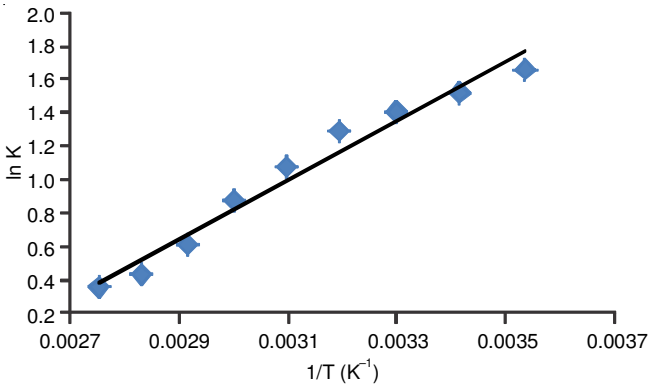


Fig. 13. Efect of temperature on adsorption of Zn(II) on to ion imprinted polymer

TABLE-3
VALUES OF CHANGE IN GIBBS FREE ENERGY (ΔG) AT DIFFERENT TEMPERATURES

| Temp. (K) | ΔG (KJ $mol^{-1}$) | Temp. (K) | ΔG (KJ $mol^{-1}$) |
|---|---|---|---|
| 238 | -4.19 | 333 | -2.27 |
| 293 | -3.78 | 343 | -1.89 |
| 303 | -3.40 | 353 | -1.52 |
| 313 | -3.03 | 363 | -1.14 |
| 323 | -3.03 | – | – |

## Conclusion

Molecularly imprinted polymers are highly crossed linked polymers that can bind certain targets with high specificity. In the present study molecularly imprinted polymer was prepared by radical polymerization. The adsorption was comparatively fast and equilibrium condition was established within 40 min. The fast establishment of adsorption equilibrium is most possibly due to high complication and geometric attraction between Zn(II) ions and Zn(II) cavities in the polymer structure. The sorption data followed quantitatively Fruendlich, Langmuir and Dubinin-Radushkevich isotherms. Maximum adsorption capability was calculated and found that the best regression coefficient was of Langmuir isotherm. The values of thermodynamic parameters ΔH, ΔS and ΔG specified that the adsorption process was exothermic and spontaneous in nature and the interactions between adsorbate and adsorbent is thermodynamically favourable. The evaluation of adsorption kinetics suggests that it obeys pseudo first order Lagergren equation.

## ACKNOWLEDGEMENTS

This work was supported by Dr. M.A. Kazi Institute of Chemistry, Univrsity of Sindh, Jamshoro, Pakistan.

## REFERENCES

1. X. Wang, Z. Xu, N. Bing and Z. Yang, *Chin. J. Chem. Eng.*, **15**, 595 (2007); https://doi.org/10.1016/S1004-9541(07)60130-X.
2. J. Otero-Romaní, A. Moreda-Piñeiro, P. Bermejo-Barrera and A. Martin-Esteban, *Microchem. J.*, **93**, 225 (2009); https://doi.org/10.1016/j.microc.2009.07.011.
3. C.D. Karlsson, Casarett and Doull's Toxicology: The Basic Science of Poisons, vol. 1236, McGraw-Hill, New York (2013).
4. T. Jiang, L. Zhao, B. Chu, Q. Feng, W. Yan and J.-M. Lin, *Talanta*, **78**, 442 (2009); https://doi.org/10.1016/j.talanta.2008.11.047.
5. C.M. Lok and R. Son, *Int. Food Res. J.*, **16**, 127 (2009);
6. D. Kumar, R. Madhuri, M.P. Tiwari, P. Sinha and B.B. Prasad, *Adv. Mater. Lett.*, **2**, 294 (2011); https://doi.org/10.5185/amlett.indias.207.
7. X. Lu, M. Kruatrachue, P. Pokethitiyook and K. Homyok, *Sci. Asia*, **30**, 93 (2004); https://doi.org/10.2306/scienceasia1513-1874.2004.30.093.
8. S. Veli and B. Alyüz, *J. Hazard. Mater.*, **149**, 226 (2007); https://doi.org/10.1016/j.jhazmat.2007.04.109.
9. B. Lesniewska, B. Godlewska-Zylkiewicz and A.Z. Wilczewska, *Microchem. J.*, **105**, 88 (2012); https://doi.org/10.1016/j.microc.2012.08.014.
10. Z.C. Li, H.T. Fan, Y. Zhang, M.X. Chen, Z.Y. Yu, X.Q. Cao and T. Sun, *Chem. Eng. J.*, **171**, 703 (2011); https://doi.org/10.1016/j.cej.2011.05.023.
11. H.T. Fan, J.Z. Li, C. Li and T. Sun, *Appl. Surf. Sci.*, **258**, 3815 (2012); https://doi.org/10.1016/j.apsusc.2011.12.035.
12. X. Luo, S. Luo, Y. Zhan, H. Shu, Y. Huang and X. Tu, *J. Hazard. Mater.*, **192**, 949 (2011); https://doi.org/10.1016/j.jhazmat.2011.05.042.
13. N.A. Yusof, A. Beyan, M.J. Haron and N.A. Ibrahim, *Sains Malays.*, **39**, 829 (2010).
14. G.Z. Memon, M.I. Bhanger, M. Akhtar, F.N. Talpur and J.R. Memon, *Chem. Eng. J.*, **138**, 616 (2008); https://doi.org/10.1016/j.cej.2007.09.027.
15. M.D. Monier, M. Ayad, Y. Wei and A.A. Sarhan, *Biochem. Eng. J.*, **51**, 140 (2010); https://doi.org/10.1016/j.bej.2010.06.007.
16. Y. Liu, Z. Liu, J. Gao, J. Dai, J. Han, Y. Wang, J. Xie and Y. Yan, *J. Hazard. Mater.*, **186**, 197 (2011); https://doi.org/10.1016/j.jhazmat.2010.10.105.
17. A.O. Dada, A.P. Olalekan, A.M. Olatunya and O. Dada, *ISOR J. Appl. Chem.*, **3**, 38 (2012).
18. Z. Xu, W. Zhang, B. Pan, C. Hong, L. Lv, Q. Zhang, B. Pan and Q. Zhang, *J. Colloid Interface Sci.*, **319**, 392 (2008); https://doi.org/10.1016/j.jcis.2007.12.015.
19. K. Yang and B. Xing, *Chem. Rev.*, **110**, 5989 (2010); https://doi.org/10.1021/cr100059s.
20. L. Zhang, S. Yang, T. Han, L. Zhong, C. Ma, Y. Zhou and X. Han, *Appl. Surf. Sci.*, **263**, 696 (2012); https://doi.org/10.1016/j.apsusc.2012.09.143.
21. C.S. Gulipalli, B. Prasad and K.L. Wasewar, *J. Eng. Sci. Technol.*, **6**, 586 (2011).
22. H. Yavuz, R. Say and A. Denizli, *Mater. Sci. Eng.*, **25**, 521 (2005); https://doi.org/10.1016/j.msec.2005.04.005.
23. M. Andaç, R. Say and A. Denizli, *J. Chromatogr. B Analyt. Technol. Biomed. Life Sci.*, **811**, 119 (2004); https://doi.org/10.1016/S1570-0232(04)00667-1.
24. P. Saha and S. Chowdhury, Insight into Adsorption Thermodynamics, INTECH Open Access Publisher, pp. 349 (2011).
25. L. Zhou, C. Shang, Z. Liu, G. Huang and A.A. Adesina, *J. Colloid Interface Sci.*, **366**, 165 (2012); https://doi.org/10.1016/j.jcis.2011.09.069.